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<p>(54) Title: FLUOROPOLYMER LOW REFLECTING LAYERS FOR PLASTIC LENSES AND DEVICES</p>			
<p>(57) Abstract</p> <p>A one or two layer coating system has been developed for plastic substrates. The one coating system low reflecting layer consists of VF₂/TFE/HFP. In the two coating system is the upper coating layer consists of TFE/HFP, VF₂/TFE/HFP, or TFE/Perfluorodioxole, and the lower coating layer consists of VF₂/TFE/HFP, VF/TFE/HFP, VAc/TFE/HFIB, or TFE graft to PVOH. A new fluoropolymer composition was prepared for use in the coating systems, prepared by the copolymerization of vinyl acetate, tetrafluoroethylene, and hexafluoroisobutylene.</p>			

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TITLEFLUOROPOLYMER LOW REFLECTING LAYERS
FOR PLASTIC LENSES AND DEVICESFIELD OF INVENTION

5 The present invention relates to fluoropolymer coated plastics. More specifically, it relates to fluoropolymer coated plastics having good adhesion, low reflective properties, and water and oil repellency.

TECHNICAL BACKGROUND

10 Much work has been done concerning low reflective plastics, particularly for plastic lenses and optical devices. One method used is vapor disposition of oxidized metal on the surface of the plastic. However, this method uses a batch process and when the substrate is large, the productivity becomes low. Another way is to apply a coating of fluoropolymer solutions. The coating is done by a dipping process and is applicable for large substrates with high productivity.

15 Though fluoropolymers have low reflective indexes, they also have very poor adhesion with plastic substrates. Improvement in the adhesion between fluoropolymers and substrate plastics has been long sought. The purpose of this invention is to provide the technology for low reflective index and good adhesion using fluoropolymer solutions.

20 SUMMARY OF THE INVENTION

The one layer coating system provided by the present invention consists of a fluorinated copolymer having the formula



25 wherein the molar ratio of Tetrafluoroethylene (TFE) to Hexafluoropropylene (HFP) is between 0.3 and 1.9, and the VF_2 content is preferably 12 to 50 mole % for PMMA substrates and 18 to 50 mole % for PC, PET, and PS substrates. More preferred is where the molar ratio of TFE to HFP is between 0.9 and 1.9, and the 30 VF_2 content is preferably 12 to 40 mole % for Polymethylmethacrylate (PMMA) substrates and 18 to 40 mole % for Polycarbonate (PC), Polyethyleneterephthalate (PET), and Polysulfone (PS) substrates.

In the case of the present invention the two-layer coating system developed for PMMA, PC, PET, and PS substrates comprises an upper layer 35 selected from the group consisting of:

a) poly(TFE/HFP) and poly($VF_2/TFE/HFP$), wherein the molar ratio of HFP to TFE is between about 0.3 and 1.9 and, in the case of the $VF_2/TFE/HFP$ terpolymer, the concentration of VF_2 is about 19 mole %; and

b) poly(TFE/perfluoro-2,2-dimethyldioxole) wherein the concentration of the perfluorodimethyldioxole is between 60 and 90 mole %; and a lower coating layer selected from the group consisting of:

5 a) poly(VF₂/TFE/HFP) wherein the ratio of TFE to HFP is between about 0.3 and 1.9 and the concentration of VF₂ is between about 18 and 60% on PMMA substrates and between about 12 and 40 mole % on PC, PET, and PS substrates;

10 b) poly(VF/TFE/HFP) wherein the ratio of TFE to HFP is between about 2.1 and 0.9 and the concentration of VF is between about 42 and 58 mole %;

15 c) poly(VAc/TFE/HFIB) wherein the concentration of VAc is between 36 and 69 mole % and the concentration of HFIB is between 14 and 52 mole %; and

d) TFE graft to PVOH wherein about 46 mole % TFE has been grafted to the PVOH.

More preferred is where the ratio of TFE to HFP is between about 0.9 and 1.9 in both the lower and upper layer, and wherein the concentration of VF₂ is between about 12 and 40 mole % when PC, PET, and PS substrates are utilized.

20 In the one layer coating system of the present invention, the thickness of the coating is preferably between about 10 and 1000 nm, more preferably, between about 30 and 120 nm, and most preferably between about 70 and 120 nm.

25 In the two coat system, the thickness of the upper layer is preferably between 10 and 1000 nm. More preferably, it is between 30 and 120 nm and most preferably, it is between 70 and 120 nm.

Another aspect of the invention is a new fluoropolymer composition prepared by the polymerization of vinyl acetate (VAc, CH₃-C(O)-OCH=CH₂), tetrafluoroethylene (TFE, CF₂=CF₂), and hexafluoroisobutylene (HFIB, (CF₃)₂C=CH₂).

30 DETAILED DESCRIPTION OF THE INVENTION

Both one layer and two layer systems have been found that afford low reflection coatings on optically clear plastic substrates. Preferred substrates are PMMA, PC, PET, and PS.

35 The one layer coating system provided by the present invention consists of a fluorinated copolymer having the formula



wherein the molar ratio of TFE to HFP is between 0.3 and 1.9 and the VF₂ content is preferably 12 to 50 mole % for PMMA substrates and 18 to 50 mole % for PC, PET, and PS substrates. These compositions balance the high fluorine content needed for low reflection, the high HFP content needed for optical clarity, and a sufficient VF₂ content to afford good adhesion to the substrate. More preferred is where the molar ratio of TFE to HFP is between 0.9 and 1.9, and the VF₂ content is preferably 12 to 40 mole % for PMMA substrates and 18 to 40 mole % for PC, PET, and PS substrates.

Although many polymers have a high enough fluorine content to perform well as a low reflection coating, they often fail because of inadequate bonding to substrates such as PMMA, PC, PET, and PS. This adhesion problem has been solved by going to systems in which a lower adhesive coat bonds a low-reflective top coat to the substrate. In the case of the present invention the two-layer coating system developed for PMMA, PC, PET, and PS substrates consists of fluoropolymers having the formulas

Upper coating layer:

Poly(TFE/HFP) and poly(VF₂/TFE/HFP), wherein the molar ratio of HFP to TFE is between about 0.3 and 1.9 and, in the case of the VF₂/TFE/HFP terpolymer, the concentration of VF₂ is about 19 mole %

or

poly(TFE/perfluoro-2,2-dimethyldioxole) wherein the concentration of the perfluorodimethyldioxole is between 60 and 90 mole %

Lower coating layer:

Poly(VF₂/TFE/HFP) wherein the ratio of TFE to HFP is between about 0.3 and 1.9 and the concentration of VF₂ is between about 18 and 60% on PMMA substrates and between about 12 and 50 mole % on PC, PET, and PS substrates

or

Poly(VF/TFE/HFP) wherein the ratio of TFE to HFP is between about 2.1 and 0.9 and the concentration of VF is between about 42 and 58 mole %

or

Poly(VAc/TFE/HFIB) wherein the concentration of VAc is between 36 and 69 mole % and the concentration of HFIB is between 14 and 52 mole %

or

A TFE graft to PVOH wherein about 46 mole % TFE has been grafted.

More preferred is where the ratio of TFE to HFP is between about 0.9 and 1.9 in both the lower and upper layer, and wherein the concentration of VF₂ is between about 12 and 40 mole % when PC, PET, and PS substrates are utilized.

The purpose of the lower layer in the present invention is to bond highly-fluorinated, low-reflection polymers to higher-reflection, hydrocarbon-polymer substrates. In order to be an effective adhesive agent, the polymer used for the adhesive layer combines perfluorocarbon monomers such as TFE and HFP with either partially fluorinated or hydrocarbon comonomers such as VF₂, HFIB, and VAc.

10 In the one layer coating system of the present invention, the coating needs to be thicker than about 10 nm in order to observe a significant reduction in reflectivity. While thicknesses greater than 10 nm work well, practical problems eventually arise as the coating is made thicker. For example, above about 1000 nm, thickness variation can become a problem, and, if the coating polymer 15 is expensive, economics start to be prohibitive. Thus, in the one layer coating system of the present invention, the thickness of the coating is preferably between about 10 and 1000 nm, more preferably, between about 300 and 120 nm, most preferably, between about 70 and 120 nm.

20 In the two layer coating system of the present invention the thickness of the upper layer can be between 10 and 1000 nm. More preferably, it is between about 30 and 120 nm, most preferably between about 70 and 120 nm. The coating process for the present invention can include any process known in the art, including but not limited to dipping, spray, or spin coating method using polymer.

25 Another aspect of the invention is a new fluoropolymer composition prepared by the copolymerization of vinyl acetate (VAc, CH₃-C(O)-OCH=CH₂), tetrafluoroethylene (TFE, CF₂=CF₂), and hexafluoroisobutylene (HFIB, (CF₃)₂C=CH₂). The polymer can be produced using any free-radical polymerization method known in the art, including but not limited to bulk, 30 solution or dispersion polymerization, using either nonaqueous or aqueous solvents. A preferred method is dispersion polymerization. Preferred solvents are water and tert-butanol/methyl acetate mixture. Dispersing agents can optionally be used; a preferred initiator is Vazo[®]52. The polymer can further be hydrolyzed, partially or completely, to provide a vinyl alcohol containing 35 copolymer.

The polymer can be recovered from the reaction using any conventional procedure such as filtration, followed by washing and drying. The polymer product can be readily dissolved in many solvents such as acetone and used for

casting films and surface coatings having the advantageous properties of fluoropolymers. One particular use is for preparing coatings having low reflective properties.

5 The following non-limiting Examples are meant to illustrate the invention but are not intended to limit it in any way.

Materials and Methods

The following definitions are used herein and should be referred to for claim interpretation.

- 10 APS – Ammonium persulfate
 HFIB – Hexafluoroisobutylene, $(CF_3)_2C=CH_2$
 HFP – Hexafluoropropylene, $CF_2=CF-CF_3$
 PC - Polycarbonate
 PET – Polyethyleneterephthalate
 PMMA - Polymethylmethacrylate
15 PVOH – Polyvinyl alcohol
 PS - Polysulfone
 Teflon® AF - TFE/Perfluoro-2,2-dimethyldioxole copolymer
 TFE – Tetrafluoroethylene, $CF_2=CF_2$
 VAc – Vinyl acetate, $CH_3-C(O)-OCH=CH_2$
20 VF – Vinyl fluoride, $CH_2=CHF$
 VF₂ – Vinylidene fluoride, $CF_2=CH_2$

Unless otherwise indicated, the following test methods were used:

Method of measuring transmission

- 25 Light transmission was measured at 500 nm using a Shimadzu #UV-3100 Spectrometer. This machine measures a continuous comparison of a split beam, part of which passes through the sample.

Adhesion Test Method

- 30 A tool with 10 razor blades separated by a distance of 1 mm was used to cut the coating down to the plastic substrate, drawing the razor blade tool first in one direction and then a second time in a perpendicular direction. This cuts 100 crosshatched squares. Scotch tape was applied to the crosshatched area with moderate pressure and pulled off rapidly. Adhesion is scored as the number of squares out of 100 still attached to the substrate.

- 35 Unless otherwise indicated, all other polymers and monomers were obtained are commercially available.

The VF₂/TFE/HFP terpolymers and the TFE/HFP dipolymers used in the present invention are compositions chosen for optical clarity and solubility. They were prepared by polymerization at 14,000 psi and 200-400°C as described in

U.S. Patent Nos. 5,478,905 and 5,637,663. This method of polymerization gives higher HFP contents and different monomer sequences than polymerizations run under ordinary emulsion and bulk polymerization methods known in the art, see for instance, *Encyclopedia of Polymer Science and Engineering*, 1989, Vol. 16, 5 pg 601-613 and Vol. 7, pg. 257-269, John Wiley & Sons. VF₂/TFE/HFP and TFE/HFP compolymers made by these more conventional methods may also work in our application as long as high fluorine content, optical clarity and easy solution coatability can be maintained.

10 PVOH grafted with TFE was prepared as in U.S. Patent No. 5,847,048, hereby incorporated by reference. The polymer contained about 46 mole % TFE groups grafted to the vinyl alcohol.

The VAc/TFE/HFIB terpolymers were prepared as described in Examples 36 to 45 below.

EXAMPLES

EXAMPLES 1-9

COMPARATIVE EXAMPLES 1-3

One Coat Poly(VF₂/TFE/HFP) on PMMA

Preferred Thickness Range

15 Solutions, 2 wt % poly(VF₂/TFE/HFP) in Fluorinert® FC-75, were made by agitating chunks of the polymer with solvent for several days at room 20 temperature. PMMA plates measuring 2.5 cm by 5.0 cm by 3 mm thick were used for testing. The PMMA plates were coated by lowering the plates into the polymer solution at a rate of 300 mm/min. and then, 30 seconds later, raising the plates back out of the solution at 2.5 to 1000 mm/min. After 5-10 minutes air 25 drying, the plates were dried horizontally for 60 minutes in a 100°C air oven. Examples are in order of increasing coating thickness.

TABLE 1
Single Coat of 18.7/43.3/38.0 mole % Poly(VF₂/TFE/HFP) on PMMA

	<u>Thickness (nm)</u>	<u>Transmittance (%)</u>
Comp. #1	Uncoated PMMA control	92.1
Comp. #2	5.0	92.8
Example #1	20.0	94.5
Example #2	70.6	96.7
Example #3	76.3	97.7
Example #4	90.2	98.0
Example #5	106.2	96.6
Example #6	133.3	93.2
Example #7	209.2	94.6

Example #8	394.7	95.2
Example #9	572.1	94.4
Comp. #3	2000	not uniform

Uncoated PMMA showed 92.1% transmission. Coatings thicker than 20.0 nm and thinner than 1000 nm gave improved transmission (>93%) relative to uncoated PMMA. The highest transmissions (>96%) were shown by coatings ~30 to 120 nm thick.

EXAMPLES 10-13

COMPARATIVE EXAMPLES 4-5

One Coat Poly(VF₂/TFE/HFP) on PMMA

Preferred VF₂ Content

10 Polymer films were prepared as in Examples 1 to 9. Transmittance and adhesion were measured with the results shown in Table 2 below which lists Examples and Comparative Examples in order of increasing VF₂ content.

TABLE 2
Adhesion by Standard Tape Pull Test
Single Coat Poly(VF₂/TFE/HFP) on PMMA

	Mole % VF ₂ /TFE/HFP	Adhesion (/100)	Transmittance (%)
Comp. #1	Uncoated PMMA control	--	92.1
Comp. #4	0/57/43 Control	0	97.2
Comp. #5	7.8 /60.3/31.8	64	97.5
Example #10	12.6/51.3/36.1	96	97.2
Example #11	18.7/43.3/18.0	99	97.9
Example #12	25.2/42.9/31.9	100	95.1
Example #13	37.4/28.9/33.7	100	96.0

15 Simultaneous good adhesion (>96/100) and improved transmission (>97%) relative to uncoated PMMA were observed for VF₂/TFE/HFP polymers with 12 to 50 mole % VF₂.

EXAMPLE 14

A solution, 2 wt % poly(VF₂/TFE/HFP = 46.9/13.5/39.6 mole %) in 20 Vertrel® XF, were made by agitating chunks of the polymer with solvent for several days at room temperature. PMMA plates measuring 2.5 cm by 5.0 cm by 3 mm thick were used for testing. The PMMA plates were coated by lowering the plates into the polymer solution at a rate of 300 mm/min. and then, 30 seconds later, raising the plates back out of the solution at 50 mm/min. After 25 5-10 minutes air drying, the plates were dried horizontally for 60 minutes in a

100°C air oven. Transmittance and adhesion were measured with the results shown the table below which lists Examples.

TABLE 3
Single Coat of 46.9/13.5/39.6 mole % Poly(VF₂/TFE/HFP) on PMMA

	Mole %'s VF ₂ /TFE/HFP	Adhesion (/100)	Transmittance (%)
Example #14B	46.9/13.5/39.6	100	97.4
Comp. #1	Uncoated PMMA control	--	92.1

5 Simultaneous good adhesion (100/100) and improved transmission (>97%) relative to uncoated PMMA were observed for VF₂/TFE/HFP = 46.9/13.5/39.6 mole % terpolymer.

EXAMPLES 15-18

COMPARATIVE EXAMPLES 6-8

10 Two Coats, Poly(VF₂/TFE/HFP) and Poly(HFP/TFE), on PMMA

Preferred VF₂ Content

15 Solutions, 1 wt % poly(VF₂/TFE/HFP) with 0-40% VF₂ in Fluorinert® FC-75, and with 4-55 mole % VF₂ in acetone were made by agitating chunks of the polymer with solvent for several days at room temperature. PMMA plates measuring 2.5 cm by 5.0 cm by 3 mm thick were used for testing. The PMMA plates were coated by lowering the plates into the polymer solution at a rate of 300 mm/min. and then, 30 seconds later, raising the plates back out of the solution at 50 mm/min. After 5-10 minutes air drying, the plates were dried horizontally for 60 minutes in a 100°C air oven. Examples and Comparative Examples are listed in order of increasing.

20 VF₂ content in the poly(VF₂/TFE/HFP) primer coat was varied. A 57 mole % TFE/43 mole % HFP top coat was used for all samples with a poly(VF₂/TFE/HFP) primer coat. Transmittance and adhesion were measured with the results shown in Table 4 below which lists the Examples and Comparative Examples in order of increasing thickness.

TABLE 4
 Two Coat. Poly(VF₂/TFE/HFP) and Poly(HFP/TFE) on PMMA
 Preferred VF₂ Content

	Mole %	Adhesion	Transmittance
	VF ₂ /TFE/HFP	(/100)	(%)
Comp. #1	Uncoated PMMA control	--	92.1
Comp. #4	0/57/43 Control	0	97.2
Comp. #6	7.8 /60.3/31.8	0	97.7
Comp. #7	12.6/51.3/36.1	4	97.5
Example #15	18.7/43.3/38.0	90	97.7
Example #16	49.3/27.7/23.0	100	97.3
Example #17	52.0/25.9/22.1	98	97.5
Example #18	61.0/21.7/17.3	80	97.4
Comp. #8	66.2/16.9/16.9	6	97.1

Good adhesion with increased transmission relative to uncoated PMMA control was observed when the poly(VF₂/TFE/HFP) primer layer had VF₂ contents between about 18 and 60 mole.

5

EXAMPLES 19-21

Two Coats both Poly(VF₂/TFE/HFP) on PMMA

Transmittance Independent of VF₂ Content of Primer Coat

Poly(VF₂/TFE/HFP) samples of different VF₂ content, see Table 5 below, were used for the primer coat. Solutions, 1 wt % poly(VF₂/TFE/HFP) in acetone, 10 were made by agitating chunks of the polymer with solvent for several days at room temperature. PMMA plates measuring 2.5 cm by 5.0 cm by 3 mm thick were used for testing. The PMMA plates were coated by lowering the plates into the polymer solution at a rate of 300 mm/min. and then, immediately, raising the plates back out of the solution at 50 mm/min. After 5-10 minutes air drying, the 15 plates were dried horizontally for 60 minutes in a 100°C air oven. The topcoat, in every instance the same 18.7 mole % VF₂/43.3 mole % TFE/38.0 mole % HFP terpolymer, was prepared by the same method.

Table 5 below lists Examples and Comparative Examples in order of increasing VF₂ content.

20

TABLE 5
Two Poly(VF₂/TFE/HFP) Coats on PMMA

	Primer Coat	Mole % VF ₂ /TFE/HFP	Adhesion (/100)	Transmittance (%)
Comp. #1	Uncoated PMMA Control		---	92.1
Example 19	49.3/27.7/23.0		100	97.5
Example 20	61.0/21.7/17.3		100	97.0
Example 21	66.2/16.9/16.9		100	97.5

In spite of variation in VF₂ content from 49.3 to 66.2 mole % in the lower layer, overall transmittance is relatively unaffected. Adhesion is excellent (100/100) for VF₂ contents from 49.3 to 66.2 mole %.

5

EXAMPLES 22 TO 24

COMPARATIVE EXAMPLES 9-12

One Coat Poly(VF₂/TFE/HFP) on Polycarbonate

Preferred VF₂ Content

Poly(VF₂/TFE/HFP) terpolymer samples of different VF₂ content were 10 coated on polycarbonate (PC) sheet using the method of Example 14. The polycarbonate was manufactured by Kyoto-Jushi Seiko Co., Ltd. The polycarbonate sheets measured 2.5 cm X 5.0 cm by 3 mm thick.

Transmission and adhesion were measured with the results shown in 15 Table 6 below which lists Examples and Comparative Examples in order of increasing VF₂ content.

TABLE 6
Single Poly(VF₂/TFE/HFP) Coat on PC

	Mole %'s VF ₂ /TFE/HFP	Adhesion (/100)	Transmittance (%)
Comp. #9	Uncoated PC Control	--	87.2
Comp. #10	0/57/43	0	95.2
Comp. #11	7.8/60.3/31.8	0	90.5
Comp. #12	12.6/51.3/36.1	53	94.7
Example #22	18.7/43.3/38.0	70	94.0
Example #23	25.2/42.9/31.9	100	92.0
Example #24	37.4/28.9/33.7	100	93.8

VF₂ contents between about 18 and 40 mole % give improved adhesion (>70/100) relative to HFP/TFE copolymer (0/100) and improved transmission 20 (>92%) relative to uncoated PC (87.2%).

EXAMPLES 25-28COMPARATIVE EXAMPLES 13 TO 14

Two Coats on Polycarbonate

Preferred VF₂ Content for Primer

5 Poly(VF₂/TFE/HFP) samples of different VF₂ content, see Table 7 below, were used for the primer coat. Solutions, 1 wt % poly(VF₂/TFE/HFP) in acetone, were made by agitating chunks of the polymer with solvent for several days at room temperature. PC plates (Kyoto-Jushi Seiko Co., Ltd.) measuring 2.5 cm by 5.0 cm by 3 mm thick were used for testing. The PC plates were coated by 10 lowering the plates into the polymer solution at a rate of 300 mm/min. and then, immediately, raising the plates back out of the solution at 50 mm/min. After 5-10 minutes air drying, the plates were dried horizontally for 60 minutes in a 100°C air oven.

15 The topcoat, in every instance the same 57.0 mole % TFE/43.0 mole % HFP copolymer, was prepared by the same method.

Table 7 below lists Examples and Comparative Examples in order of increasing VF₂ content.

TABLE 7
Two Coats on PC

	Primer Coat	Mole % VF ₂ /TFE/HFP	Adhesion (/100)	Transmittance (%)
Comp. #9	Uncoated PC control		--	87.2
Comp. #13	0/57/43 control		68	93.8
Comp. #14	7.8/60.3/31.8		12	91.6
Example #25	12.6/51.3/36.1		83	94.2
Example #26	18.7/43.3/38.0		96	92.3
Example #27	25.2/42.9/31.9		88	93.4
Example #28	37.4/28.9/33.7		97	93.2

20 VF₂ contents between about 12 and 40 mole % give improved adhesion (>83/100) relative to HFP/TFE dipolymer (68/100) and improved transmittance (>92.3%) relative to uncoated polycarbonate (87.2%).

EXAMPLES 29 TO 31

Two Coats on PMMA

25 Use of Poly(VF/TFE/HFP) as Primer Coat

Preferred VF Content

A stirred jacketed stainless steel horizontal autoclave of 7.6 L (2 U.S. gal) capacity was used as the polymerization vessel. The autoclave was equipped with

instrumentation to measure temperature and pressure and with a compressor that could feed monomer mixtures to the autoclave at the desired pressure. The autoclave was filled to 55-60% of its volume with deionized water containing 15 g of Zonyl® FS-62 surfactant (DuPont Co., Wilmington, DE) and heated to 5 90°C. It was then pressured to 3.1 MPa (450 psig) with nitrogen and vented three times. The autoclave was precharged with monomers in the desired ratio, as shown in the table below, and brought to the working pressure of 3.1 MPa (450 psig). Initiator solution was prepared by dissolving 2 g APS in 1 L of deionized water. The initiator solution was fed to the reactor at a rate of 10 25 mL/min for a period of five minutes and then the rate was reduced and maintained at 1 mL/min for the duration of the experiment. For Examples 36 and 38 the autoclave was operated in a batch mode. The polymerization was terminated after a 10% pressure drop was observed by venting the remaining unconverted monomers and by reducing the autoclave temperature to room 15 temperature.

For the 26.2/46.4/27.5 polymer, the autoclave was operated in a semibatch fashion in which a monomer mixture was added to the reactor to maintain constant pressure by means of the compressor as polymerization occurred. The composition of this make-up feed was different from the precharged mixture, as 20 shown in the table below, because of the differences in monomer reactivity. The composition was selected to maintain a constant monomer composition in the reactor so compositionally homogeneous product was formed. Make-up monomer feed was admitted to the autoclave, through the compressor, by means of an automatic pressure regulated valve to maintain reactor pressure. Monomer 25 feeds were continued until a predetermined amount to give the final latex solids was fed to the autoclave. The feed was then stopped and the contents of the autoclave were cooled and vented.

In all cases, the polymer latex was easily discharged to a receiver as a milky homogeneous mixture. Polymer was isolated on a suction filter after 30 adding 15 g of ammonium carbonate dissolved in water per liter of latex followed by 70 mL of HFC-4310 (1,1,1,2,3,4,4,5,5,5-decafluoropentane) per liter of latex with rapid stirring. The filter cake was washed with water and dried in an air oven at 90-100°C.

TABLE 8

Monomer Precharge TFE/VF/HFP (wt%)	Monomer Make-up TFE/VF/HFP (wt%)	Monomer Fed (g)	Polymer Comp. Solids (wt%)	Polymer (g)	TFE/VF/HFP (wt%)
15/3/82		750.9	2.1	96.6	38.3/42.8/19
9/3/88	29/46/25	1702	18.3	1063	26.2/46.4/27.5
10/10/80		636.1	2.2	99.7	20.3/57.8/22

- Poly(VF/TFE/HFP) samples of different VF content, see Table 9 below, were used for the primer coat. Solutions, 2 wt % poly(VF/TFE/HFP) in acetone, were made by agitating chunks of the polymer with solvent for several days at room temperature. PMMA plates measuring 2.5 cm by 5.0 cm by 3 mm thick were used for testing. The PMMA plates were coated by lowering the plates into the polymer solution at a rate of 300 mm/min. and then, immediately, raising the plates back out of the solution at 50 mm/min. After 5-10 minutes air drying, the plates were dried horizontally for 60 minutes in a 100°C air oven.
- The topcoat, in every instance the same 57 mole % TFE/43 mole % HFP polymer, was prepared by the same method.

Table 9 below lists Examples in order of increasing VF content.

TABLE 9
Two Coats, VF/TFE/HFP Primer, on PMMA

Primer Coat Mole %'s VF/TFE/HFP	Adhesion (/100)	Transmittance (%)
Comp. #1	Uncoated PMMA control	---
Example #29	42.8/38.3/19.0	99
Example #30	46.4/26.2/27.5	100
Example #31	57.8/20.8/22.0	100

- For VF contents from about 42 to 58 mole %, use of poly(VF/TFE/HFP) as the primer coat gives excellent transmittance (>96.0%) relative to uncoated PMMA (92.1%) along with excellent adhesion (>99/100).

EXAMPLE 32

Two Coats on PMMA

Use of Graft of TFE to PVOH as Primer Coat

A poly(vinyl alcohol) to which 46 mole % TFE had been grafted (PVOH-g-TFE) was used for the primer coat. A solution, 2 wt % in acetone, was made by agitating chunks of the polymer with solvent for several days at room temperature. PMMA plates measuring 2.5 cm by 5.0 cm by 3 mm thick were

used for testing. The PMMA plates were coated by lowering the plates into the polymer solution at a rate of 300 mm/min. and then, immediately, raising the plates back out of the solution at 50 mm/min. After 5-10 minutes air drying, the plates were dried horizontally for 60 minutes in a 100°C air oven.

5 The topcoat, an 57 mole % TFE/43 mole % HFP polymer, was prepared by the same method.

Table 10 below gives adhesion and transmission results.

TABLE 10
Two Coats, PVOH-g-TFE Primer, on PMMA

	Primer Coat PVOH-g-TFE	Adhesion (/100)	Transmittance (%)
Comp. #1	Uncoated PMMA control	--	92.1
Example #32	46 mole % TFE	97	97.1

10 Use of poly(PVOH-g-TFE) as the primer coat gave excellent transmittance (97.1%) relative to uncoated PMMA (92.1%) along with excellent adhesion (97/100).

EXAMPLE 33

COMPARATIVE EXAMPLES 15-16

15 One Coat Poly(VF₂/TFE/HFP) on PET

Coatings were prepared as in Examples 1 to 9. PET sheets measuring 2.5 by 5.0 cm by 0.12 mm thick were used as substrate. Transmittance and adhesion were measured with the results shown in the table below which lists Examples and Comparative Examples.

20

TABLE 11
Poly(VF₂/TFE/HFP) Coat on PET

	Mole %'s VF ₂ /TFE/HFP	Adhesion (/100)	Transmittance (%)
Comp. #15	Uncoated PET control	--	85.0
Comp. #16	0/57/43	2	96.0
Example #33	18.7/43.3/38.0	99	96.0

Uncoated PET showed 85.0% transmission. Simultaneous good adhesion (>99/100) and improved transmission (>96%) relative to uncoated PET were observed.

EXAMPLE 34COMPARATIVE EXAMPLE 17-18One Coat Poly(VF₂/TFE/HFP) on Polysulfone

Coatings were prepared as in Example 1 to 9. Polysulfone sheets measuring 2.5 X 5.0 cm by 0.05 mm thick were as substrate. Transmittance and adhesion results are shown in the table below which lists Examples and Comparative Examples.

TABLE 12
Single Coat Poly(VF₂/TFE/HFP) on Polysulfone

	Mole %'s VF ₂ /TFE/HFP	Adhesion (/100)	Transmittance (%)
Comp. #17	Uncoated PS	--	88.5
Comp. #18	0/57/43	97	98.2
Example #34	18.7/43.3/38.0	100	95.0

10 Uncoated polysulfone showed 88.5% transmittance. Simultaneous good adhesion (>97/100) and improved transmission (>95%) relative to uncoated polysulfone (88.5%) were observed.

EXAMPLE 35
COMPARATIVE EXAMPLE 19

15 Two coat polymer films were prepared on PMMA sheet as in Examples 15-18. A Teflon® AF top coat was used. Transmittance and adhesion were measured with the results shown in the table below which lists the Examples and Comparative Examples.

TABLE 13
Two Coats, Poly(VF₂/TFE/HFP) and Teflon® AF, on PMMA

	Mole %'s VF ₂ /TFE/HFP	Adhesion (/100)	Transmittance (%)
Comp. #1	Uncoated PMMA control	--	92.1
Comp. #19	AF1600 control (no lower coat)	0	98.1
Example #35	49.3/27.7/23.0	100	98.0

20 Adhesion was 100/100 for the two coat sheet (VF₂/TFE/HFP and Teflon® AF) but only 0/100 for the sheet with a single coating of Teflon® AF. This shows that poly(VF₂/TFE/HFP) is an effective primer that further improves the adhesion of Teflon® AF.

25 Transmittance at 500 nm was 98.0% for two coat sheet (VF₂/TFE/HFP and AF) but only 92.1 for uncoated PMMA control. This shows that Teflon® AF

is an effective top coat that further improves the transmittance of poly(VF₂/TFE/HFP).

EXAMPLES 36-45

Aqueous Polymerization of VAc/TFE/HFIB. A 1-L stirred vertical autoclave was charged with a solution of 0.3 g of Plasdone K-90 (steric stabilizer) and 5 mL isopropanol (chain transfer agent) in 400 mL of deionized water. Vinyl acetate (126 g, 1.47 mole) and 0.6 g of Vazo® 52 were added. The vessel was closed, pressurized to 100 psi with nitrogen and vented twice. The vessel was pressured to 295 psi with nitrogen as a leak test and vented. The vessel was cooled to about -4°C, evacuated and charged with 42 g (0.26 mol) of hexafluoroisobutylene and 42 g (0.42 mol) of tetrafluoroethylene. With stirring at 750 rpm, the vessel contents were heated to 70°C and maintained for 3 hr. The contents was heated to 85°C and maintained for 3 hr. After cooling to room temperature and venting to atmospheric pressure, the aqueous suspension was removed from the vessel using water as necessary to rinse. An additional 350 mL of deionized water were added and the white suspension was heated with stirring on a hot plate until about 250 mL of solution had evaporated. After cooling to room temperature, the solid was easily filtered on a sintered glass funnel and washed with deionized water. It was dried in a vacuum oven at 90°C overnight giving 181.8 g (87%) of white polymer.

Nonaqueous Polymerization of VAc/TFE/HFIB. A 1-L stirred vertical autoclave was charged with a solution of 126 g of vinyl acetate in 110 g of methyl acetate and 200 g of tert-butanol. The vessel was closed, pressurized to 100 psi with nitrogen and vented twice. The vessel was pressured to 295 psi with nitrogen as a leak test and vented. The vessel was cooled to about -4°C, evacuated and charged with 63 g of tetrafluoroethylene and 21 g of HFIB. With stirring at 750 rpm, the vessel contents were heated to 70°C. A solution (25 mL) of 0.2 g Vazo® 52 in 25 mL methyl acetate was injected at 5 ml/min. After 3 hr. the vessel contents were allowed to cool to room temperature and the remaining gases were vented. The viscous solution was removed from the vessel by suction, diluting with acetone as necessary to lower solution viscosity. The polymer solution, further diluted with acetone if necessary to give a clear solution, was added slowly in 30-45 mL portions to 16 oz of deionized water and a small amount of ice in a blender. The precipitated solid was filtered in a sintered glass funnel. After all polymer had been precipitated the combined solids were washed in portions with water, filtered and pressed with a rubber dam. The solid was dried for several hours in a vacuum oven with a slow nitrogen purge at 110-115°C. The resulting white solid weighed 141.1 g (67%).

Table 14 below gives results for polymerizations carried out by one of the methods listed above.

Vinyl acetate content was determined by hydrolysis of the acetate groups using excess of sodium hydroxide in refluxing THF, followed by titration of 5 excess base by standard hydrochloric acid solution. GPC analyses were conducted using THF as solvent and polystyrene standards. Elemental analyses were done by Schwarkoff Microanalytical Laboratory. ^{19}F NMR spectra were generally measured in THF-d6 solutions using TMS and CFC-11 as internal standards. ^{19}F NMR was used to assign relative amounts of the two fluorinated 10 monomers from integration of the CF_3 groups of HFIB at -66 to -70 versus the CF_2 groups from TFE at -110 to -126.

TABLE 14

Ex.	Monomers (g)	Weight Ratio Feed/Products ^a	Polym. Solv. ^b	Reactor	Yield, g (%)	Wt. % VAc	F NMR (mole %)	Refractive Index	Inph. Visc.	% FC	GPC	M _w /M _n /PD
36	VAc (52) TFE (30) HFIB (49)	40:23:37 (39:13:48)	t-BuOH MeAc	400 mL	94.6 (72)	39.0	TFE 31% HFIB 69%	1.4111	0.41	38.92	148,000 84,900 1.75	
37	VAc (86) TFE (50) HFIB (82)	39:23:38 (36:12:52)	Water PVP	1 L	175.6 (81)	35.5	TFE 28% HFIB 72%	1.4169	0.38	36.70	177,000 82,500 2.15	
38	VAc (103) TFE (40) HFIB (66)	49:19:32 (50:12:38)	Water PVP	1 L	182.5 (87)	50.2	TFE 33% HFIB 67%	1.4191	0.52	31.09	252,000 81,800 3.08	
39	VAc (126) TFE (42) HFIB (42)	60:20:20 (58:16:26)	Water ^d PVP	1 L	181.8 (87)	58.1	TFE 50% HFIB 50%	1.4307	0.79	22.95	349,000 120,000 2.90	
40	VAc (126) TFE (63) HFIB (21)	60:30:10 (69:19:12)	Water ^d PVP	1 L	172.9 (82)	68.6	TFE 73% HFIB 27%	1.4368	1.98	20.83	786,000 208,000 3.77	
41	VAc (147) TFE (42) HFIB (21)	70:20:10 (71:16:13)	Water ^d PVP	1 L	186.3 (89)	70.7	TFE 65% HFIB 34%	1.4439	2.01	17.69	857,000 243,000 3.52	
42	VAc (126) TFE (63) HFIB (21)	60:30:10 (62:24:14)	t-BuOH MeAc	1 L	141.1 (67)	61.5	TFE 74% HFIB 26%	1.4284	0.78	26.22	235,000 100,000 2.33	
43	VAc (126) TFE (42) HFIB (42)	60:20:20 (57:15:27)	t-BuOH MeAc	1 L	148.4 (71)	57.2	TFE 48% HFIB 52%	1.4198	0.59	29.83	204,000 116,000 1.76	

Ex.	Monomers (g)	Weight Ratio Feed/Product ^a	Polym. Solv. ^b	Reactor	Yield, g (%)	Wt. % VAc	F NMR (mole %)	Refractive Index	Inh. Visc.	% I ^c	GPC	Mw/ Mn/PDI
44	VAc (147) TFE (42) HFIB (21)	70:20:10 (66:19:15)	t-BuOH MeAc	1 L	142.5 (68)	66	TFE 68% HFIB 32%	1.4353	0.78	22.33	230,000 126,000	1.82
45	VAc (147) TFE (42) HFIB (21)	70:20:10 (69:17:14)	Water PVP	1 L	187.1 (89)	68.8	TFE 68% HFIB 32%	1.4422	1.09	17.83	437,000 145,000	3.0

^a Vinyl acetate content determined by hydrolysis of the acetate groups using standard base, fluoromonomer incorporation was determined by ¹⁹F NMR. ^b Polyvinyl pyrrolidone (0.3 g) used as dispersing agent and isopropanol (5 mL) used as chain transfer agent in aqueous polymerizations. ^c Elemental analysis. ^d No chain transfer agent used.

EXAMPLES 46-48

Two Coats on PMMA

Use of Poly(VAc/TFE/HFIB) as Primer Coat

Preferred VAc Content

5 Poly(VAc/TFE/HFIB) samples of different VAc content, see Table 9 below, were used for the primer coat. Solutions, 2 wt % poly(VAc/TFE/HFIB) in acetone, were made by agitating chunks of the polymer with solvent for several days at room temperature. PMMA plates measuring 2.5 cm by 5.0 cm by 3 mm thick were used for testing. The PMMA plates were coated by lowering the plates
10 into the polymer solution at a rate of 300 mm/min. and then, immediately, raising the plates back out of the solution at 50 mm/min. After 5-10 minutes air drying, the plates were dried horizontally for 60 minutes in a 100°C air oven.

The topcoat, in every instance the same 57 mole % TFE/43 mole % HFP polymer, was prepared by the same method.

15 Table 15 below lists Examples and in order of increasing VAc content.

TABLE 15
 Two Coats, VAc/TFE/HFIB Primer, on PMMA

Comp. #1	Primer Coat		
	Mole % VAc/TFE/HFIB	Adhesion (/100)	Transmittance (%)
Uncoated PMMA control	---	---	92.1
Example #46 36/12/52	100	100	96.8
Example #47 58/16/26	100	100	97.6
Example #48 69/17/14	100	100	97.3

For VAc contents from about 36 to 69 mole %, use of poly(VAc/TFE/HFIB) as the primer coat gives excellent transmittance (>96.8%)
20 relative to uncoated PMMA (92.1%) along with excellent adhesion (100/100).

What is claimed is:

1. A one layer coating system for coating a substrate comprising a fluorinated copolymer having the formula

5

$\text{VF}_2/\text{TFE}/\text{HFP}$

wherein the molar ratio of TFE to HFP is between 0.9 and 1.9 and the VF_2 content is about 12-40%.

2. The coating system of Claim 1 wherein the VF_2 content is 12 to 10 40 mole % and the substrate is PMMA.
3. The coating system of Claim 1 wherein the VF_2 content is 18 to 40 mole % and the substrate is selected from the group consisting of PC, PET, and PS.
4. The coating of Claim 1 wherein the thickness of the coating is 15 between 10 nm and 1000 nm.
5. The coating of Claim 4 wherein the thickness of the coating is between 70 nm and 120 nm.
6. A two-layer coating system for coating substrates selected from the group consisting of PMMA, PC, PET, and PS comprising an upper layer selected 20 from the group consisting of:
 - a) poly(TFE/HFP) and poly($\text{VF}_2/\text{TFE}/\text{HFP}$), wherein the molar ratio of HFP to TFE is between about 0.9 and 1.9 and, in the case of the $\text{VF}_2/\text{TFE}/\text{HFP}$ terpolymer, the concentration of VF_2 is about 19 mole %; and
 - b) poly(TFE/perfluoro-2,2-dimethyldioxole) wherein the 25 concentration of the perfluorodimethyldioxole is between 60 and 90 mole %, and a lower coating layer selected from the group consisting of:
 - a) poly($\text{VF}_2/\text{TFE}/\text{HFP}$) wherein the ratio of TFE to HFP is between about 0.9 and 1.9 and the concentration of VF_2 is between about 18 and 60% on PMMA substrates and between about 12 and 40 mole % on PC, PET, and PS 30 substrates;
 - b) poly($\text{VF}/\text{TFE}/\text{HFP}$) wherein the ratio of TFE to HFP is between about 2.1 and 0.9 and the concentration of VF is between about 42 and 58 mole %;
 - c) poly(VAc/TFE/HFIB) wherein the concentration of VAc is 35 between 36 and 69 mole % and the concentration of HFIB is between 14 and 52 mole %; and
 - d) TFE graft to PVOH wherein about 46 mole % TFE has been grafted to the PVOH.

7. The two layer coating system of Claim 6 wherein the thickness of the lower coating layer is less than 20 nm.

8. The two layer coating system wherein the thickness of the upper layer is 10 nm to 1000 nm.

5 9. The two layer coating system of Claim 8 wherein the thickness of the upper layer is between 70 nm and 120 nm.

10. A composition prepared by the polymerization of vinyl acetate (VAc, $\text{CH}_3\text{-C(O)-OCH=CH}_2$), tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$), and hexafluoroisobutylene ($(\text{CF}_3)_2\text{C=CH}_2$).

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



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(54) Title: FLUOROPOLYMER LOW REFLECTING LAYERS FOR PLASTIC LENSES AND DEVICES

(57) **Abstract:** A one or two layer coating system has been developed for plastic substrates. The one coating system low reflecting layer consists of VF₂/TFE/HFP. In the two coating system the upper coating layer consists of TFE/HFP, VF₂/TFE/HFP, or TFE/Perfluorodioxole, and the lower coating layer consists of VF₂/TFE/HFP, VF/TFE/HFP, VAc/TFE/HFIB, or TFE graft to PVOH. A new fluoropolymer composition was prepared for use in the coating systems, prepared by the copolymerization of vinyl acetate, tetrafluoroethylene, and hexafluoroisobutylene.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/07263

A. CLASSIFICATION OF SUBJECT MATTER	IPC 7 C09D127/12 C08J7/04 B05D7/26 C08F214/26 C08F218/08
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D C08J C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 798 158 A (KOIKE MASAKI ET AL) 25 August 1998 (1998-08-25) claims 1,5 ---	1
X	EP 0 050 436 A (DU PONT) 28 April 1982 (1982-04-28) claims 1-4; example 24 ---	1
X	EP 0 889 066 A (DU PONT) 7 January 1999 (1999-01-07) claims; example 89 ---	1
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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& document member of the same patent family

Date of the actual completion of the international search 31 October 2000	Date of mailing of the international search report 14.12.2000
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/07263

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199632 Derwent Publications Ltd., London, GB; Class A14, AN 1996-317814 XP002151596 & JP 08 142280 A (FUKUBI KAGAKU KOGYO KK), 4 June 1996 (1996-06-04) abstract ---	8,9
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 00/07263

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-5

One layer coating comprising terpolymer of VF2/TFE/HFP with the molar ratio of TFE to HFP between 0.9-1.9 and VF2 being 12-40%

2. Claims: 6-7

Two layer coating comprising terpolymer of VF2/TFE/HFP with the molar ratio of HFP to TFE between 0.9-1.9 and VF2 being 12-40%

3. Claims: 8-9

Two layer coating having specific thickness without taking reference to coating composition of claim 6-7 more 1-5

4. Claim : 10

Composition prepared by polymerisation of vinyl acetate, tetraethylene and hexafluoroisobutylene.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/07263

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